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<b>(54) Title: AQUATHERMOLYTIC CLEAVAGE OF UNSATURATED KETONES</b>  <b>(57) Abstract</b>  The present invention provides a simplified process for converting unsaturated ketones having from 6 to about 24 carbon atoms into the corresponding saturated ketones comprising forming an aqueous mixture of the unsaturated ketone and at least about 50 % by weight water and heating the mixture under autogeneous pressure at a temperature of from about 200 to 450 °C, more preferably from about 250 °C up to the critical temperature of water which is about 374 °C. Heating is continued for a period of time sufficient to convert at least about 20 % by weight of the unsaturated ketone, usually from about 5 up to about 120 minutes, depending on temperature, the amount of water present and the identity of the starting ketone feedstock. The process may be characterized as an aquathermolysis reaction wherein the reaction proceeds in water primarily through ionic routes rather than through free radical routes. Accordingly, relatively high conversion rates and good yields of saturated ketone and other reaction by-products may be obtained without the necessity of using a catalyst in the process.		

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AQUATHERMOLYTIC CLEAVAGE  
OF UNSATURATED KETONES

This application is related to copending application Serial No. 07/852,438, filed March 16, 1992 which is a Continuation-In-Part of application Serial No. 07/411,121, filed September 22, 1989, now abandoned.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process for cleaving unsaturated ketones to saturated ketones of lower molecular weight by aquathermolysis chemistry.

Description of Related Art

Unsaturated ketones such as mesityl oxide and phorone are considered to be higher value materials with varied uses such as solvents, paint formulations, insect repellents and intermediates for organic synthesis. However, many unsaturated ketones are formed as by-products during the synthesis of simpler saturated ketones or aldehydes and, as such, constitute impurities of little commercial value which must be separated out of the reaction mixture and disposed of. For example, aldol condensation of methyl ethyl ketone (MEK) formed during the zinc oxide-catalyzed oxidation of

sec-butyl alcohol leads to the formation of alpha, beta unsaturated keto dimers (and higher oligomers) which may concentrate in the MEK distillation residue at levels of up to 50% by weight. Of this amount, approximately 45% by weight constitutes unsaturated C<sub>8</sub> ketones and the balance comprises a mixture of higher ketones, saturated ketones and olefins. The presence of these materials in reactor heavies severely restricts the further application of such heavier residuums for uses such as motor fuels or further refining. In addition, the added costs associated with separation of these materials severely detracts from overall process efficiency and economics. Accordingly, such bottoms are usually disposed of by burning.

It is known in the prior art that unsaturated ketones such as mesityl oxide or pulegone can be converted to the corresponding saturated ketone, e.g., acetone, by a hydrolysis reaction promoted using a catalyst. For Example, U.S. Patent 4,766,249 discloses the hydrolysis of an unsaturated carbonyl compound of the formula  $R'R''C=R$  to produce a carbonyl-containing compound of the formula  $R'-CO-R''$  and  $H_2R$ , by conducting the hydrolysis under reflux conditions in the presence of a catalytic amount of hydroxide ion and at a pH of 11-13. Specifically claimed is the hydrolysis of pulegone to yield a mixture of acetone and 3-methylcyclohexanone.

Japanese patent document JP 54/70,210 discloses the preparation of acetone from mesityl oxide by

heating a product which contains mesityl oxide with aqueous alkali at temperatures equal or greater than 80°C for a period of time equal to or greater than 10 minutes.

Netherlands patent document NL 72/6,875 teaches a similar process wherein mesityl oxide is converted to acetone by the catalytic reaction of mesityl oxide with water in the presence of cyclohexylamine and benzoic acid at 93°C for 10 minutes.

While these and similar processes are generally effective and efficient insofar as they go, they all suffer from the requirement that catalysts are used in the processes. In commercial processes, the presence of significant levels of acidic or basic catalyst materials in the production of liquids and gases may give rise to corrosion problems with respect to production equipment and additional production expense with respect to the disposition of acidic or basic effluents in an environmentally acceptable manner.

#### SUMMARY OF THE INVENTION

The present invention provides a simplified process for converting unsaturated ketones having from 6 to about 24 carbon atoms into the corresponding saturated ketones comprising forming an aqueous mixture of the unsaturated ketone and at least about 50% by weight water and heating the mixture under autogeneous pressure at a temperature of from about 200° to 450°C, more preferably from about 250°C

up to the critical temperature of water which is about 374°C. Heating is continued for a period of time sufficient to convert at least about 20% by weight of the unsaturated ketone, usually from about 5 up to about 120 minutes, depending on temperature, the amount of water present and the identity of the starting ketone feedstock.

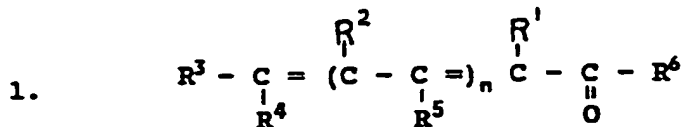
The process may be characterized as an aquathermolysis reaction wherein the reaction proceeds in water primarily through ionic routes rather than through free radical routes. Accordingly, relatively high conversion rates and good yields of saturated ketone and other reaction by-products may be obtained without the necessity of using a catalyst in the process.

#### DETAILED DESCRIPTION OF THE INVENTION

The present invention is based on the discovery that alpha, beta or beta, gamma unsaturated bonds in unsaturated ketones may be cleaved in an aqueous medium. The ionic reaction mechanism is facilitated largely as a consequence of the favorable changes that occur in the chemical and physical properties of water at temperatures between about 200°C up to and above the critical temperature of water which is about 374°C. These changes are manifest by water which has a higher dissociation constant, a lower density and a lower dielectric constant. These properties generally increase the solubility of the ketones in water and help facilitate ionic reaction pathways in aqueous

systems, such that water serves as both a reaction medium and a source of ions.

Unsaturated ketones which may be converted in accordance with the process of this invention include phorone and other alpha, beta unsaturated ketones having the formula 1:

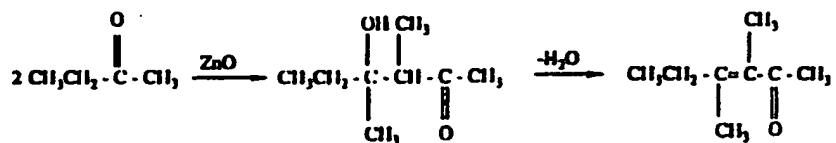


wherein R<sup>1</sup> and R<sup>2</sup> are selected from the group consisting of hydrogen and an alkyl group containing from 1 to about 4 carbon atoms, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup>, and R<sup>6</sup> are alkyl groups containing from 1 to about 4 carbon atoms and n is 0, 1 or 2. The process is equally applicable for the conversion of beta, gamma unsaturated ketones which are isomers of compounds having the general structure of formula 1, as well as mixtures of alpha, beta and beta, gamma unsaturated ketones.

Inclusive of unsaturated ketones within the scope of formula 1 are mesityl oxide and other unsaturated keto oligomers which are formed as by-products during the oxidation of sec-alkyl alcohols to form the corresponding ketones. These unsaturated ketones generally contain from 6 to about 24 carbon atoms.

For example, acetone may be commercially produced by the oxidation of isopropyl alcohol using a suitable dehydrogenation catalyst such as zinc

oxide. Methyl ethyl ketone (MEK) is produced by a similar process involving the oxidation of sec-butyl alcohol. During these oxidation steps, substantial quantities of unsaturated dimer and higher ketones are formed as a consequence of difficult-to-control Aldol condensation reactions. In the case of acetone manufacture, mesityl oxide may be formed as a major by-product as the result of aldol condensation of two molecules of acetone during the oxidation step. During the manufacture of MEK, dimer ketones are formed as the major by-product in accordance with the following reaction scheme:



In accordance with this invention, these Aldol condensation products as well as other alpha, beta, or beta, gamma unsaturated ketones such as phorone may be readily converted to the corresponding saturated ketones by the aquathermolytic process disclosed herein wherein water serves as both the reaction medium and the catalytic source of protons and hydroxy ions.

Although ordinary tap water may be used in the process, it is preferred to use distilled or deionized water substantially free of dissolved



salts and particularly preferred to use water which has been deoxygenated and is substantially free of dissolved oxygen. Removal of oxygen tends to minimize the occurrence of free radical side reactions during the process.

The amount of water used in forming the mixture with the unsaturated ketone may generally range from at least about 50% by weight up to about 97% by weight, i.e., the mixture may contain from about 1 to 30 parts by weight water per part by weight of unsaturated ketone. In general, the higher the water content of the mixture within the above specified range, the greater the conversion of the unsaturated ketone at any given process temperature within the 200 to 450°C range. Conversely, the higher the process temperature within the range, the less water is required to give rise to higher conversion rates of the ketone. The preferred water content of the mixture ranges from about 2 to about 15 parts by weight of water per part ketone, with 2 to 10 parts by weight of water being most preferred.

As indicated above, the process is conducted by introducing the water and unsaturated ketone into a reaction vessel and heating the mixture under autogeneous pressure and preferably in an inert atmosphere, such as argon or nitrogen, as an aid in excluding oxygen from the system, and at a preferred temperature within the range of from about 250 to 450°C for a period of time such that a least about 20% by weight of the unsaturated ketone

is cleaved at the double bond(s) and converted into other products. Normally, the process is conducted at a temperature not higher than the critical temperature of water which is about 374°C, but supercritical temperatures above that and up to about 450°C may also be utilized. Good results in terms of the percentage of unsaturated ketone converted and yield of saturated ketone realized are achieved with process temperatures within the range of from about 300 to 374°C.

Acceptable conversion rates of at least about 20% by weight may be achieved by conducting the reaction over a time period of as little as 5 minutes up to 120 minutes or more. At higher temperatures and/or with higher water/ketone ratios, less time is required to achieve good conversion rates and vice versa. Most preferably the water content and reaction temperatures are such as to achieve conversion rates of at least about 50% by weight within 10 to 60 minutes, more preferably within 10 to 30 minutes.

The term "autogeneous pressure of the system" refers to the combined vapor pressure exerted by the mixed components present in the aqueous system heated at a particular process temperature. The autogeneous pressure of water alone in such a system ranges from about 600 to 3200 psia over a temperature range of from about 250°C up to about 374°C. Obviously, the autogeneous pressure of a system containing both water and the unsaturated ketone would be higher over this temperature range

as a function of the ketone content and the partial pressure exerted by the ketone.

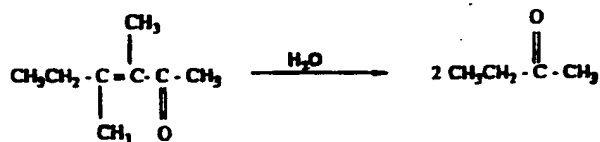
Since it is believed that the reaction process of this invention proceeds largely via an ionic reaction mechanism in the aqueous medium, it is not necessary and indeed undesirable from the environmental standpoint to include catalyst components in the reactant mixture. Thus, in the preferred embodiment, the reaction mixture "consists of" a mixture of water and unsaturated ketone composition. However, in some cases it may be desirable to add small quantities of a stronger or weaker acid or base to the reaction mixture, since it has been found that the presence of the acid or base enhances the ionic reaction mechanism and generally gives rise to higher rates of conversion of the ketone starting material.

Thus, in a second embodiment of the invention, the reaction mixture may "consist essentially of" a mixture of water and unsaturated ketone and may further include appropriate amounts of a strong or weak acid to adjust the pH of the reaction mixture in the range of from just below 7.0 down to about 2.0, or appropriate amounts of a strong or weak base to adjust the pH of the reaction mixture in the range of from just above 7.0 up to about 14.0. Suitable acids include phosphoric, acetic, hydrochloric or sulfuric acids; suitable bases include alkali metal hydroxides or carbonates. It has been generally found that aquathermolysis conducted in the presence of an acid or base tends

to speed up the conversion process and leads to higher yields of the desired saturated ketone product because of the presence of additional protons or hydroxide ions in the system.

The reaction mixture may also include small quantities of an ionic surfactant stable at higher temperatures to assist in enhancing the dispersibility of the unsaturated ketone in the water, particularly where higher molecular weight ketones are present. Preferred surfactants include anionic surfactants such as sodium lauryl sulfonate.

The term "conversion" as used herein is defined as effective C=C bond cleavages (hydration of the double bond followed by cleavage of the molecule at the former site of the double bond) in unsaturated ketones to produce more desirable value added chemical compounds. For example, aquathermolysis of one mole of aldolized MEK dimer yields two moles of MEK in accordance with the following reaction scheme:



The percentage conversion of the starting unsaturated ketone which may be achieved in accordance with the process of this invention may

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generally range from at least about 20%, preferably at least about 50% up to 100%, depending upon reaction conditions.

The process of the present invention may be particularly adapted for use in conjunction with other chemical processes wherein unsaturated ketones are formed as a less valuable by-product as described above. For example, MEK is produced commercially by the hydration of n-butylene to sec-butyl alcohol followed by oxidation of the alcohol over a ZnO catalyst to form a reaction product which comprises a mixture of MEK and unsaturated aldolized MEK dimers and heavier products.

After separation of MEK by distillation, the residuum (bottoms) which contains the unsaturated ketones may be mixed with water and subjected to aquathermolysis in accordance with this invention to produce additional MEK.

The process of this invention may be carried out batchwise or in the continuous mode using conventional pressure equipment. Examples of such equipment include a laboratory bomb, a high pressure autoclave, a stirred tank reactor or a continuous flow-through tube, each equipped with a heating means capable of achieving and maintaining the required temperatures and pressures over the required time period.

The following examples are illustrative of the invention.

EXAMPLE 1

A laboratory-prepared unsaturated C<sub>8</sub> ketone was synthesized by reacting methyl ethyl ketone over Amberlite™ IRA-400 base ion exchange resin in a Soxhlet extractor to form the Aldol condensation product. The aldol product was then converted to the unsaturated C<sub>8</sub> ketone by heating it and distilling it over an acidic ion exchange catalyst (Amberlyst™ 15) to provide a product having a molecular weight of 126. Mass spectrometric and C<sup>13</sup> NMR analyses showed the product to contain primarily cis and trans alpha, beta isomers in which the C=C bond is conjugated with the C=O bond. This ketone corresponds to a product of the structure of formula 1 above wherein R<sup>1</sup>, R<sup>4</sup> and R<sup>6</sup> are each methyl, R<sup>3</sup> is ethyl and n is 0. The product was also found to contain lesser amounts of cis and trans beta, gamma isomers where the double bond was not conjugated with the carbonyl group.

Into an 11 cc capacity stainless steel reactor bomb were placed 0.55 g of the unsaturated ketone product prepared above and 5.0 g of deoxygenated distilled water. The reactor was sealed under nitrogen and the reactor was heated in a sand bath at 315°C for 60 minutes. The reactor was then cooled to room temperature.

Unconverted ketone was extracted from the reaction mixture with toluene using a known amount of pentadecane as an internal standard. This extract as well as the converted ketone (MEK) remaining in

the aqueous medium were analyzed by gas chromatography which showed that 99% of the unsaturated ketone was converted with a selectivity of 100% to MEK, as shown in Table 1. Selectivity is based on the stoichiometry with two moles of MEK formed per mole of unsaturated C<sub>8</sub> ketone.

#### EXAMPLES 2-8

A number of additional experiments were conducted in accordance with the process of Example 1 at 315°C except that the reaction times and weight ratio of water to unsaturated C<sub>8</sub> ketone were varied as shown in Table 1. Also, the reaction mixture of Examples 5 and 6 included 3% by weight of acetic acid and 3% by weight of sodium hydroxide respectively. The reaction in Example 8 was conducted without the presence of water, i.e., 100% unsaturated ketone was used. Results are shown in Table 1.

TABLE 1

	<u>H<sub>2</sub>O/C<sub>8</sub></u> <u>(w/w)</u>	<u>Time</u>	<u>% Conv.</u>	<u>MEK Select</u> <u>(Mole%)</u>
Ex. 1	10/1	60	99	100
Ex. 2	10/1	30	96	100
Ex. 3	5/1	60	98	100
Ex. 4	2/1	60	84	100
Ex. 5	2/1 (3% HAC)	60	91	100
Ex. 6	2/1 (3% NaOH)	60	98	100
Ex. 7	1/1	60	73	100
Ex. 8	0	60	3	100

Analysis of the above data shows that an excess of

water is required to achieve high conversion to MEK, with almost no reaction occurring in the absence of water as shown in Example 8. Somewhat higher rates of conversion are obtained with acidic or basic water as illustrated by a comparison of Example 4 and Examples 5 and 6 respectively. The selectivity to MEK was 100% regardless of % conversion or the relative acidity or basicity of the water employed.

#### EXAMPLE 9

Example 1 was repeated exactly as set forth except that the ketone composition mixed with the water was a heavy ketone bottoms product obtained from the MEK distillation residue of a commercial MEK manufacturing process. This residue contained about 42% by weight of mixed unsaturated C<sub>8</sub> ketone isomers as well as smaller amounts of saturated C<sub>8</sub> ketones and C<sub>10</sub>, C<sub>11</sub>, and C<sub>12</sub> - cyclohexene-ones.

Analysis of the reaction product showed an MEK yield of 0.81 g per 1.0 g of unsaturated C<sub>8</sub> ketone present in the reaction mixture, which corresponds to 0.35 g. of MEK per 1.0 g of the starting bottoms product. Selectivity to MEK was about 80 mole %. The saturated ketones and C<sub>10</sub>, C<sub>11</sub>, and C<sub>12</sub> cyclohexene-ones did not revert to MEK.

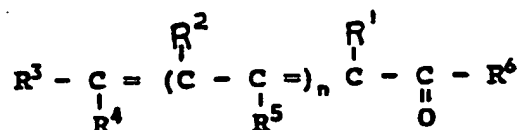


## CLAIMS:

1. A process for converting alpha, beta or beta, gamma unsaturated ketones having at least 6 carbon atoms into the corresponding saturated ketones comprising forming an aqueous mixture comprising said unsaturated ketone and at least about 50% by weight water, heating said mixture in a closed system at a temperature within the range of from about 200°C up to about 450°C under the autogeneous pressure of the system and for a period of time sufficient to convert at least about 20% by weight of said unsaturated ketone, and recovering said saturated ketone.

2. The process of claim 1 wherein said unsaturated ketones contain from 6 to about 24 carbon atoms.

3. The process of claim 2 wherein said unsaturated ketones comprise alpha, beta unsaturated ketones having the formula:



wherein R<sup>1</sup> and R<sup>2</sup> are selected from the group consisting of hydrogen and an alkyl group containing from 1 to about 4 carbon atoms, R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are alkyl groups containing from 1 to

about 4 carbon atoms and n is 0, 1 or 2.

4. The process of claim 3 wherein  $R^1$ ,  $R^4$  and  $R^6$  are each methyl,  $R^3$  is ethyl and n is 0.

5. The process of claim 1 wherein said aqueous mixture contains up to about 30 parts by weight water per part by weight unsaturated ketone.

6. The process of claim 5 wherein said aqueous mixture contains from about 2 to about 15 parts by weight water per part by weight of unsaturated ketone.

7. The process of claim 1 wherein said mixture is heated at a temperature of up to about 374°C.

8. The process of claim 7 wherein said mixture is heated at a temperature of from about 250°C up to about 374°C.

9. The process of claim 7 wherein said aqueous mixture is heated for a period of time of from about 5 to about 120 minutes.

10. The process of claim 9 wherein said aqueous mixture is heated for a period of time of from about 10 to about 60 minutes.

11. The process of claim 1 wherein said aqueous mixture further contains an acid sufficient to develop a pH in the range of just below 7.0 down

to about 2.0.

12. The process of claim 1 wherein said aqueous mixture further contains a base sufficient to develop a pH in the range of just above 7.0 up to about 14.0.

13. The process of claim 1 wherein said aqueous mixture consists of said water and said unsaturated ketone.

14. The process of claim 1 wherein said unsaturated ketone is selected from the group consisting of mesityl oxide, phorone and the Aldol condensation product of methylethyl ketone.

15. The process of claim 14 wherein said unsaturated ketone is the aldol condensation product of methylethyl ketone and said recovered saturated ketone is methylethyl ketone.

16. The process of claim 1 wherein said water is deoxygenated water.

## INTERNATIONAL SEARCH REPORT

Inter- national Application No

PCT/US 93/07331

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 5 C07C45/67 C07C45/54 C07C45/28

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 5 C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US,A,4 709 098 (J.E. DOLFINI ET AL.) 24 November 1987 see the whole document ----	1-9,16
X	DE,C,875 512 (FARBENFABRIKEN BAYER) 19 March 1953 see the whole document -----	1,11
X	DE,C,946 443 (FARBENFABRIKEN BAYER) 12 July 1956 see the whole document -----	1,12

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

17 November 1993

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Information on patent family members

International Application No

PC1/US 93/07331

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-4709098	24-11-87	AU-A- 1363588	24-08-88
		EP-A- 0346383	20-12-89
		JP-A- 63301841	08-12-88
		WO-A- 8805771	11-08-88
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		US-A- 4927805	22-05-90
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DE-C-875512		NONE	
DE-C-946443		NONE	